The University of Chicago

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A Dissertation Submitted to the Faculty of the
Division of the Physical Sciences in Candidacy
for the Degree of Doctor of Philosophy

Department of Physics

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The Specific Isotope Effect in the Hyperfine Spectrum of the Lead Atom

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(Received August 17, 1934)

A calculation by the method of Hughes and Eckart is performed for the specific isotope separation of Pb^{206} and Pb^{208} levels for terms arising from the $6p^2$, $6p7s$, $6p6d$, $6p7d$ and $6p8s$ configurations. The electron wave functions used are an ortho-normal set having the effective nuclear charge as parameter. From the perturbation calculation a double sum is obtained. Slater's method of sums is used to remove the degeneracy existing in the magnetic quantum number. The double sums for the various configurations of lead are found to contain a great number of terms which are common for all configurations and only a few terms which differ for the various configurations. These terms which are different for the various configurations are calculated and summed to obtain a "net specific isotope separation." It is found that an effective nuclear charge of only about 55 is necessary to make this net specific isotope separation equal to the observed isotope separation. A small variation from term to term of the same configuration requires that some other effect also be postulated. An upper limit argument for the specific isotope separation leads to a result of the order of thousands of wave numbers. This is shown to result from the vast number of terms in the double sum. It is not to be expected that this high upper limit for the separation would be approached by the actual separation. A set of wave functions which would be accurate enough to permit evaluating and subtracting the double sums does not seem obtainable.

1. CALCULATION OF THE SPECIFIC ISOTOPE SEPARATION USING ORTHOGONAL FUNCTIONS

THE effect of the motion of the nucleus upon the spectrum of an atom having more than one orbital electron has been discussed by Hughes and Eckart.[1] The results which they obtained for the two and three electron systems were in good numerical agreement with the measured values of isotope displacements in the Li I and Li II spectra. Recently Bartlett and Gibbons[2] calculated the isotope shifts for singlet and triplet levels in the Ne I spectrum. In this paper it is proposed to apply the method of Hughes and Eckart to the calculation of isotope displacements in the spectrum of the Pb-atom.

The kinetic energy operator for an atomic system of N electrons and one nucleus is given by Hughes and Eckart in the following form:

$$T=-\hbar^2\left\{\sum_{k=1}^{N}[\nabla_k/2\mu]+\sum_{(k,\,j)}[\nabla_k\cdot\nabla_j/M]+[\nabla^2/2(M+Nm)]\right\}, \quad (1)$$

in which

$$\nabla_k=\mathbf{i}\partial/\partial x_k+\mathbf{j}\partial/\partial y_k+\mathbf{k}\partial/\partial z_k,$$
$$\nabla=\mathbf{i}\partial/\partial X+\mathbf{j}\partial/\partial Y+\mathbf{k}\partial/\partial Z,$$

x_k, y_k, z_k = coordinates of the kth electron for which the origin is located at the moving nucleus,

X, Y, Z = coordinates of the center of mass of the atom in an arbitrary system with fixed origin,

m = electronic mass,

M = nuclear mass,

$\mu=mM/m+M$ = reduced electronic mass.

The third term in the bracket of Eq. (1) is the kinetic energy operator for the motion of the center of mass of the atom. Since this motion is of no significance in the calculation of isotope effects, the third term may be dropped from the bracket. The first and second terms of the bracket give rise respectively to the normal isotope effect and to the specific isotope effect. Hughes and Eckart have discussed the calculation of the normal isotope effect for any atom and have shown that it may be accomplished by multiplying the term values for a stationary nucleus by the fraction μ/m.

The second term in the bracket, which accounts for the specific isotope effect, may be used as a perturbing term for the calculation of the energy displacement. The degeneracy existing in the magnetic quantum number is not taken into account in the perturbation calculation. Instead the problem is solved assuming no degeneracy and the method of sums of Slater is used to remove the degeneracy existing in the

[1] D. S. Hughes and Carl Eckart, Phys. Rev. **36**, 694 (1930).
[2] J. H. Bartlett and J. J. Gibbons, Phys. Rev. **44**, 538 (1933).

magnetic quantum number. In the event that the unperturbed wave function has been normalized the result of such calculation is:

$$\Delta W = \sum_{(k,\,j)} \Delta W_{kj}, \tag{2}$$

where

$$\Delta W_{kj} = \int u^*(-\hbar^2 \nabla_k \cdot \nabla_j / M) u d\tau. \tag{3}$$

The form of the wave function which it is intended to use is the one given by Slater[3]:

$$u = (1/N!) det[\psi(n_1|x_1)\psi(n_2|x_2) \cdots \psi(n_N|x_N)], \tag{4}$$

where $$\psi(n|x) = R(nl|r)\, Y(lm|\theta\phi)\Xi(s|\sigma). \tag{5}$$

It is assumed that the ψ's form an ortho-normal set and hence it may be shown that u, as defined above, is normalized and that[4]

$$\Delta W_{kj} = (-1/M)|\mathbf{P}(n_k; n_j)|^2, \tag{6}$$

where $\mathbf{P}(n_k; n_j)$ is the vector momentum matrix element associated with the transition from orbit n_k to orbit n_j. As is well known, it may be expressed in terms of the corresponding coordinate matrix element:

$$\mathbf{P}(n_k; n_j) = (im/\hbar)(W_k - W_j)\mathbf{X}(n_k; n_j). \tag{7}$$

By using the substitution of the coordinate elements and the wave functions in a spherically symmetric field it is possible to perform the integration for ΔW_{kj}. The summation over the spin functions results in a delta-function of the spin quantum numbers. The integral of the spherical harmonics is well known from the calculation of intensity for a simple rotator:

$$\beta(k; j) = (X^2 + Y^2 + Z^2)/[r(k; j)]^2, \tag{8}$$

where

$$\Delta l = +1 \begin{cases} \Delta m = +1 & |X|^2 = |Y|^2 = \frac{1}{4}\dfrac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}[r(k;j)]^2 \quad |Z|^2 = 0, \\ \Delta m = 0 & |Z|^2 = \dfrac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}[r(k;j)]^2 \quad |X|^2 = |Y|^2 = 0, \\ \Delta m = -1 & |X|^2 = |Y|^2 = \frac{1}{4}\dfrac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}[r(k;j)]^2 \quad |Z|^2 = 0. \end{cases} \tag{9}$$

The expressions for $\Delta l = -1$ may be obtained from the foregoing, and all others are zero. The quantity $r(k; j)$ in these expressions is the integral of the radial functions:

$$r(k; j) = \int_0^\infty R(n_k l_k|r) R(n_j l_j|r) r^3 dr. \tag{10}$$

The resulting expression for the specific isotope displacement is in terms of wave numbers:

$$\Delta\nu = \sum_{(k,\,j)} \{-RmZ^4 \cdot [n_j^2 - n_k^2]^2 \cdot \delta(s_k; s_j) \cdot \beta(k; j) \cdot [r(k; j)]^2 / 2Ma^2 n_k^4 n_j^4\}. \tag{11}$$

The radial integrals contain a common factor a/Z, in which a is the radius of the first Bohr orbit and Z is the nuclear charge. This leaves $\Delta\nu$ in Eq. (11) dependent upon the square of the nuclear charge.

The degeneracy in the perturbation calculation, which has been ignored in obtaining Eq. (11) for the specific isotope displacement, may be removed by Slater's method of sums. The result of the calculation by the method of sums is to correlate $\Delta\nu$ for any spectroscopic term with $\Delta\nu$ for an electronic configuration. For the purpose of discussing the electron configurations numbers have been assigned to the electrons starting with the innermost. Electrons having a spin of $+\frac{1}{2}$ are allotted the odd numbers while electrons having a spin of $-\frac{1}{2}$ are allotted the even numbers. The serial numbers are assigned encyclopedically from the quantum numbers nlm, in the order of increasing n and l and decreasing m. For example, number 6 is $n=2$, $l=1$, $m=1$, $s=\frac{1}{2}$ while number 61 is $n=5$, $l=0$, $m=0$, $s=\frac{1}{2}$. The single number system of designation is much more compact than the four quantum number system for writing the complicated lead configurations.

[3] J. C. Slater, Phys. Rev. **34**, 1293 (1929).
[4] For evaluation of the perturbation matrix refer to C. Eckart, Rev. Mod. Phys. **2**, 375 (1930).

In the normal lead atom there are four electrons outside of the completed $5n$ shell. Two of these electrons are fixed in the $6s$ shell for all of the configurations considered, so that it is only the two outermost electrons (numbered from 81 up) which will differ in the various configurations. This leads to an important simplification in Eq. (11). The summation over all pairs of electrons k and j contains a great many terms which will be common for all configurations. It is only when k (and/or j) is numbered greater than 80 that a term will occur in the summation which will not be a common term for all configurations. The common terms give rise to an additive constant in the term-values which is of no significance since it cannot be observed, the frequencies being differences between two term-values.

With this simplification it is now possible to state the result of the calculation by the method of sums assuming that the coupling is Russell-Saunders. The specific isotope displacement for one Russell-Saunders term has the form:

$$\Delta\nu(6p^2\ {}^1D)=\Delta\nu(81, 82), \tag{12}$$

in which $\Delta\nu(81, 82)$ is the result of the summation of Eq. (11) using for k the electrons numbers 81 and 82 and for j all electrons numbers 1, 2, $\cdots$, 80, 81, 82. The other Russell-Saunders terms require similar summations:

$$\Delta\nu(6p^2\ {}^3P) =\Delta\nu(81, 83), \tag{13}$$

$$\Delta\nu(6p^2\ {}^1S) =\Delta\nu(81, 86)+\Delta\nu(83, 84)+\Delta\nu(85, 82)-\Delta\nu(85, 86)-\Delta\nu(82, 84), \tag{14}$$

$$\Delta\nu(6p7s\ {}^3P)=\Delta\nu(81, 97), \tag{15}$$

$$\Delta\nu(6p7s\ {}^1P)=\Delta\nu(81, 98)+\Delta\nu(82, 97)-\Delta\nu(81, 97), \tag{16}$$

$$\Delta\nu(6p6d\ {}^3F)=\Delta\nu(81, 87), \tag{17}$$

$$\Delta\nu(6p6d\ {}^3D)=\Delta\nu(81, 89)+\Delta\nu(83, 87)-\Delta\nu(81, 87), \tag{18}$$

$$\Delta\nu(6p7d\ {}^3F)=\Delta\nu(81, 105), \tag{19}$$

$$\Delta\nu(6p7d\ {}^3D)=\Delta\nu(81, 107)+\Delta\nu(83, 105)-\Delta\nu(81, 105), \tag{20}$$

$$\Delta\nu(6p8s\ {}^3P)=\Delta\nu(81, 115), \tag{21}$$

$$\Delta\nu(6p8s\ {}^1P)=\Delta\nu(81, 116)+\Delta\nu(82, 115)-\Delta\nu(81, 115). \tag{22}$$

In Table I the summation is performed for the cases in which k of Eq. (11) is one of the orbital electrons numbered greater than 80. Instead of calculating the summations for an isotope of mass M, the table is calculated in terms of the difference in $\Delta\nu$ for the Pb^{206} and Pb^{208} isotopes. These isotopes give rise to very strong lines in the hyperfine spectrum which are not complicated by the effect of nuclear spin. A simple calculation will show that the normal isotope separation of spectroscopic levels for the two will be insignificant. Since actual separations are observed for term levels in the hyperfine spectrum, it is desirable to compare the observed separations with the sums calculated from Eq. (11). The nuclear charge is left as an undetermined parameter in the calculations.

Most of the integrals $r(k; j)$ for this table were evaluated by Kupper.[5] However, two additional integrals are necessary to complete the table:

$$[r(6p; nd)]^2=\frac{2^{19}3^9n^9(n^2-1)(n^2-4)(n-6)^{2n-14}}{5\ 7\ (n+6)^{2n+14}}\{-475n^6+23{,}364n^4-353{,}808n^2+1{,}632{,}960\}^2, \tag{23}$$

$$[r(6p; ns)]^2=\frac{2^{15}3^7n^9(n-6)^{2n-14}}{5\ 7\ (n+6)^{2n+14}}\times\{-2761n^8+132{,}528n^6-2{,}057{,}184n^4+11{,}757{,}312n^2-19{,}595{,}520\}^2. \tag{24}$$

With the summations performed in this table it is possible to find the separations of the Pb^{206} and the Pb^{208} isotope levels in the lead spectrum. Such isotope separations have been measured by many experimenters[6–9] in connection with

[5] A. Kupper, Ann. d. Physik **86**, 511 (1928).
[6] H. Schuler and G. Jones, Zeits. f. Physik **75**, 565 (1932).
[7] H. Kopfermann, Zeits. f. Physik **75**, 363 (1932).
[8] J. Rose and L. Granath, Phys. Rev. **40**, 775 (1932).
[9] K. Murakawa, Scientific Papers (Tokyo), Nos.: 191, 245, 367, 372, 398.

TABLE I.

Orbitals k	j	$\beta(k;j)$	$[r(k;j)]^2$	$10^6(\Delta\nu^{208}-\Delta\nu^{206})/Z^2$
81	1	1/3	0.0241	10.54
	3	1/3	0.292	6.69
	11	1/3	1.856	5.97
	19	2/5		
	21	1/5	0.0757	.049
	23	1/15		
	29	1/3	11.98	6.67
	37	2/5		
	39	1/5	1.263	1.41
	41	1/15		
	61	1/3	49.2	3.41
	69	2/5		
	71	1/5	15.3	2.12
	73	1/15		
				Total = 37.30
83	1	1/3	0.0241	10.54
	3	1/3	0.292	6.69
	11	1/3	1.856	5.97
	21	1/5		
	23	4/15	0.0757	0.49
	25	1/5		
	29	1/3	11.98	6.67
	39	1/5		
	41	4/15	1.263	1.41
	43	1/5		
	61	1/3	49.2	3.41
	71	1/5		
	73	4/15	15.3	2.12
	75	1/5		
				Total = 37.30
87	5	2/5	0.438	12.06
	13	2/5	3.03	11.71
	31	2/5	19.3	12.90
	47	3/7		
	49	1/7	0.32	0.34
	51	1/35		
	63	2/5	231.	19.20
				Total = 56.21
89	5	1/5	0.438	12.06
	7	1/5		
	13	1/5	3.03	11.71,
	15	1/5		
	31	1/5	19.3	12.90
	33	1/5		
	49	2/7		
	51	8/35	0.32	0.34
	53	3/35		
	63	1/5	231.	19.20
	65	1/5		
				Total = 56.21

Orbitals k	j	$\beta(k;j)$	$[r(k;g)]^2$	$10^6(\Delta\nu^{208}-\Delta\nu^{206})/Z^2$
97	5	1/3		
	7	1/3	0.01414	1.03
	9	1/3		
	13	1/3		
	15	1/3	0.1566	1.78
	17	1/3		
	31	1/3		
	33	1/3	1.38	3.36
	35	1/3		
	63	1/3		
	65	1/3	35.0	18.70
	67	1/3		
	81	1/3	1560.	39.30
				Total = 64.17
105	5	2/5	0.2416	7.10
	13	2/5	1.439	6.58
	31	2/5	6.68	6.60
	47	3/7		
	49	1/7	0.080	0.19
	51	1/35		
	63	2/5	35.8	7.80
	81	2/5	408.	12.34
				Total = 40.61
107	5	1/5	0.2416	7.10
	7	1/5		
	13	1/5	1.439	6.58
	15	1/5		
	31	1/5	6.68	6.60
	33	1/5		
	49	2/7		
	51	8/35	0.080	0.19
	53	3/35		
	63	1/5	35.8	7.80
	65	1/5		
	81	1/5	408.	6.17
				Total = 34.44
115	5	1/3		
	7	1/3	0.00886	0.68
	9	1/3		
	13	1/3		
	15	1/3	0.0887	1.12
	17	1/3		
	31	1/3		
	33	1/3	0.598	1.83
	35	1/3		
	63	1/3		
	65	1/3	4.13	3.43
	67	1/3		
	81	1/3	16.04	1.10
				Total = 8.16

TABLE II. *Isotopic separations in head.*

Pb term	Specific isotope separation	Net specific isotope separation	Observed isotope separation	Effective nuclear charge
$(6p^2\ ^1D)$	$74.60\ Z_1^2\ \text{cm}^{-1}$	$(74.60\ Z_1^2-101.47\ Z_4^2)$	$-0.088\ \text{cm}^{-1}$	54.4
$(6p^2\ ^3P)$	$74.60\ Z_2^2$	$(74.60\ Z_2^2-101.47\ Z_4^2)$	-0.85	54.6
$(6p^2\ ^1S)$	$74.60\ Z_3^2$	$(74.60\ Z_3^2-101.47\ Z_4^2)$	$-.077$	55.7
$(6p7s\ ^3P)$	$101.47\ Z_4^2$	0	.000	55[a]
$(6p7s\ ^1P)$	$101.47\ Z_5^2$	$(101.47\ Z_5^2-101.47\ Z_4^2)$	$-.017$	
$(6p6d\ ^3F)$	$93.51\ Z_6^2$	$(93.51\ Z_6^2-101.47\ Z_4^2)$	$-.030$	54.6
$(6p6d\ ^3D)$	$93.51\ Z_7^2$	$(93.51\ Z_7^2-101.47\ Z_4^2)$	$-.033$	54.3
$(6p7d\ F)$	$77.91\ Z_8^2$	$(77.91\ Z_8^2-101.47\ Z_4^2)$		
$(6p7d\ D)$	$59.40\ Z_9^2$	$(59.40\ Z_9^2-101.47\ Z_4^2)$	$-.241$	33.6
$(6p8s\ P)$	$45.46\ Z_{10}^2$	$(45.46\ Z_{10}^2-101.47\ Z_4^2)$	$-.017$	80.2
$(6p8s\ P)$	$45.46\ Z_{11}^2$	$(45.46\ Z_{11}^2-101.47\ Z_4^2)$		

[a] The value of Z_4 was chosen equal to 55 because this value makes the other Z's have an identical average value.

the hyperfine spectrum. Most of the results have been stated upon the assumption that the isotope separation for the $6p7s\ ^3P$ term is zero. This convention is observed in Table II, in the column headed "net specific isotope separation." The values for this column are obtained by subtraction of the calculated specific isotope separation for the $6p7s\ ^3P$ term from the calculated values for all other terms. The nuclear charge which has been left as an undetermined parameter is established in such a way as to give results for the specific isotope separations which agree with the measured values. This is accomplished by assigning to each spectroscopic term in Table II, a different nuclear charge. Upon subtracting the specific isotope separation of the $6p7s\ ^3P$ term from the specific isotope separation for all other terms the net specific isotope separation is obtained, which depends upon two values of the effective nuclear charge. If the observed isotope separations are set equal to these values of the net specific isotope separation, equations are obtained which may be plotted using the squares of the nuclear charges for ordinate and abscissa. These equations are plotted in the form of straight lines from which it is easy to show that the specific isotope separations of the terms arising from the $6p^2$ $6p7s$, $6p6d$, configurations may be calculated with remarkable accuracy by using for all Z's the value 55. Another way to handle this is to assign $Z_4=55$ for the $6p7s\ ^3P$ term and to calculate the other Z's. This is done in the last column of Table II. For the $6p7d$ and $6p8s$ configurations the terms require different values of Z.

From the last column in this table a number of important deductions may be drawn concerning the specific isotope effect. The values listed are those which Z must have to bring the calculation into numerical agreement with the observations. In the first place, all values of Z^2 come out positive, which means that the calculated separations and observed separations agree in direction. Secondly, all values of Z are less than the true value. This indicates that the effect under consideration is by no means negligible; if it were, the effective values of Z would come out very much greater than 82. Finally it is evident that the values of Z for all terms of the $6p^2$ configuration are nearly equal, as they are also for all terms arising from each of the other configurations with the exception of $6p7d$. This is probably due, at least in part, to the approximate nature of the calculation, which cannot account for the smaller variations of the separation from term to term. Nevertheless, because of this it seems necessary to postulate contributions from other causes for the separation.

For the terms arising from the $6p7d$ configuration a special condition holds. While the specific isotope separation of only one of the terms has been measured, the calculated values are quite different. The difference arises in the summation

of Eq. (11) in the term in which j is a $6p$ electron while k is a $7d$ electron. In this term the value of $\beta(k;j)$ depends upon the m-values, so that the two Russell-Saunders terms from this configuration lead to different results upon summing. This condition does not occur in the $6p6d$ configuration since $r(6p;6d)$ is zero. The condition is also not found for any configuration $6pns$ since in this case $\beta(6p;ns)$ is the same for any m-value.

2. An Upper Limit to the Specific Isotope Displacement

In the case that non-orthogonal wave functions involving different nuclear charges Z are to be used for the various orbitals the number of terms in the summation in Eq. (2) becomes very great. It is for this reason that the effective nuclear charge was considered the same for all electrons in the preceding section. However, a very interesting calculation for the maximum limit may be performed without making use of the assumption of orthogonality.

For this calculation let the wave equation of a complex atom be written:

$$(T_0+V)u=Wu, \tag{25}$$

where

$$T_0=(-\hbar^2/m)\sum_i \nabla_i^2, \tag{26}$$

$$V=\sum_i (Ne^2/r_i)+\sum_{(i,\,j)}(e^2/r_{ij}). \tag{27}$$

Now if θ is a real quantity:

$$\sum_i\sum_j \int (\nabla_i u^*+\theta\nabla_j u^*)(\nabla_i u+\theta\nabla_j u)d\tau \geq 0, \tag{28}$$

$$\sum_i\sum_j \int (\nabla_i u^*\cdot\nabla_i u+\theta\nabla_i u^*\cdot\nabla_j u+\theta\nabla_j u^*\cdot\nabla_i u + \theta^2\nabla_j u^*\cdot\nabla_j u)d\tau \geq 0. \tag{29}$$

This latter expression may be integrated by parts and the integral

$$\int \nabla^2(u^*u)d\tau$$

set equal to zero. In this way Eq. (29) may be written:

$$\sum_i\sum_j -\int (u^*\nabla_i^2 u+2\theta u^*\nabla_i\cdot\nabla_j u + \theta^2 u^*{}_j\nabla u)d\tau \geq 0. \tag{30}$$

Since the operator T_1 for the specific isotope effect is defined by:

$$T_1=(-\hbar^2/2M)\sum_i\sum_j \nabla_i\cdot\nabla_j, \tag{31}$$

then Eq. (30) becomes:

$$N\tau_0+2M\theta\tau_1/m+\theta^2 N\tau_0\geq 0, \tag{32}$$

in which τ_0 is the average value of T_0 while τ_1 is the average value of T_1. Hence the discriminant of Eq. (32) must be negative:

$$N^2\tau_0^2-M^2\tau_1^2/m^2\leq 0, \tag{33}$$

$$\tau_1\leq mN\tau_0/M. \tag{34}$$

From the theorem of the virial it may be shown that the wave-mechanical mean of the kinetic energy is equal to one-half the wave-mechanical mean of the potential energy taken with the reverse sign. This result is also true in the case that each electron is acted upon by a different field:[10]

$$2\int u^*T_0 u d\tau=-\int u^*Vud\tau. \tag{35}$$

This result makes it possible to express the mean values of potential and kinetic energy in terms of the total energy:

$$\int u^*T_0 u d\tau=-W\int u^*ud\tau, \tag{36}$$

$$\int u^*Vud\tau=2W\int u^*ud\tau. \tag{37}$$

So that

$$\tau\leq mN|W|/M. \tag{38}$$

However, since $|W|$ is the energy required to strip the atom of all electrons and is very great, the upper limit of τ_1 becomes very great. Using the K energy level for an approximate value of W leads to a separation for the energy levels of Pb^{206} and Pb^{208} isotopes of the order of thousands of wave numbers. However, this huge limit is not surprising. In the summations of Eq. (2)

[10] J. C. Slater, J. Chem. Phys. **1**, 667 (1933).

there are $N(N-1)/2\ \Delta W_{kj}$'s of which only from one to five are not common for all configurations. If the common terms were also summed the calculated magnitude of the energy level separations would be greatly increased, but would have no effect in the separation of the spectrum lines. This fact that the line-separation is the small difference of two large numbers probably accounts for the variation of the calculated effect with the choice of wave function, noted by Bartlett and Gibbons, and also encountered in attempts to refine the present calculation. In any event it is not to be expected that the separation of the isotope levels would approach this high limit, since it is merely a limit and since it is so large in comparison with observed isotope separations.

The writer wishes to thank Professor Carl Eckart for suggesting the problem and discussing its solution many times with him.

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